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Communication: Structure, formation, and equilibration of ensembles of Ag-S complexes on an Ag surface

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Communication: Structure, formation, and equilibration of ensembles of Ag-S complexes on an Ag surface

Abstract

We have utilized conditions of very low temperature (4.7 K) and very low sulfur coverage to isolate and identify Ag-S complexes that exist on the Ag(111) surface. The experimental conditions are such that the complexes form at temperatures above the temperature of observation. These complexes can be regarded as polymeric chains of varying length, with an Ag₄S pyramid at the core of each monomeric unit. Steps may catalyze the formation of the chains and this mechanism may be reflected in the chain length distribution.

Keywords

catalysis, silver, sulphur, surface chemistry, surface reconstruction, Ames Laboratory, Physics and Astronomy, Materials Science and Engineering

Disciplines

Chemistry | Materials Science and Engineering | Physics

Comments

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Communication: Structure, formation, and equilibration of ensembles of Ag-S complexes on an Ag surface

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We have utilized conditions of very low temperature (4.7 K) and very low sulfur coverage to isolate and identify Ag-S complexes that exist on the Ag(111) surface. The experimental conditions are such that the complexes form at temperatures above the temperature of observation. These complexes can be regarded as polymeric chains of varying length, with an Ag₄S pyramid at the core of each monomeric unit. Steps may catalyze the formation of the chains and this mechanism may be reflected in the chain length distribution. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790571>]

The inadequacy of the traditional picture that chemisorption and catalytic processes occur on metal surfaces which are static bystanders is now well-recognized. One manifestation of this inadequacy is the formation of intricate and sometimes beautifully ordered sulfur- and oxygen-induced reconstructions of metal surfaces.^{1–5} The reconstructions can have large, semi-three-dimensional unit cells, in which the metal atom density differs from that of the clean surface. These structures have different chemical properties than either the metal surface or the bulk oxide/sulfide surface, and can play a key role in catalysis, for example.^{2,6,7} Another manifestation of non-static metal surfaces is the existence of small metal-additive complexes that form when a clean surface is exposed to additives (such as O or S). These complexes are generally mobile and can even facilitate metal surface dynamics and mass transport across the surface.^{8–13} More specifically, these complexes can destabilize metal nanostructures and can accelerate coarsening or sintering of arrays of nanoclusters via a reactive version of Ostwald ripening.^{11,14} The modern tools of surface science—particularly scanning tunneling microscopy (STM), diffraction techniques, and density functional theory (DFT)—have proven powerful enough to decipher even intricate extended structures, but *direct* experimental observations of isolated *complexes* between adsorbates and metal atoms extracted from the surface have been limited, due in part to difficulties in imaging mobile species. Also missing from the above observations is a characterization of the formation mechanism for complexes, the possibility that there exists a variety of distinct complexes interacting with each other, and a potential connection between these complexes and extended reconstructions.

The focus of this paper is on the system S/Ag(111). In order to isolate and identify Ag-S complexes, we utilize conditions of very low temperature where complexes are likely to be immobile, and very low S coverage where complexes are unlikely to be subsumed into, or replaced by, extended reconstructions. In addition, we will provide insight into the formation and equilibration of these moieties at temperatures higher than the temperature of observation.

A partial phase diagram has been established for this system, which helps guide expectation.¹⁵ There is a ($\sqrt{7} \times \sqrt{7}$)R19° reconstruction, in which the Ag atom density is not conserved, relative to the clean surface.^{15–19} This reconstruction is stable at 135–300 K and at coverages of 0.4 ML or higher. At lower temperature and lower coverage, two other equilibrium phases exist, both of which are also thought to involve a change in Ag atom density.¹⁵ In the first, Ag₃S₃ clusters are aligned in rows and embedded in an ordered S overlayer, at coverages ranging from 0.03 to 0.3 monolayers (ML) of S at 200 K. The second phase is stable at 135 K, and consists of parallel stripes. It has been observed at 0.09 ML S, but its coverage-dependence has not been explored. Both phases disappear and reappear reversibly with thermal cycling. Overall, the richness of these phase equilibria, involving multiple phases in which Ag is displaced from lattice sites, suggests that S-Ag interactions are strongly attractive, which should favor the formation of complexes under the conditions described above.

In the present work, STM images were acquired using a low-temperature STM (Omicron GmbH) in ultra-high vacuum.²⁰ The Ag(111) sample (MaTeck GmbH) was cleaned by repeated cycles of Ar⁺ sputtering and annealing at ~670 K. S₂(gas) was generated from a solid-state electrochemical Ag|AgI|Ag₂S|Pt cell *in situ*.²¹ Sulfur coverage was determined by comparing STM image areas with prior data, in which Auger electron spectroscopy was implemented as an absolute measure.¹⁵

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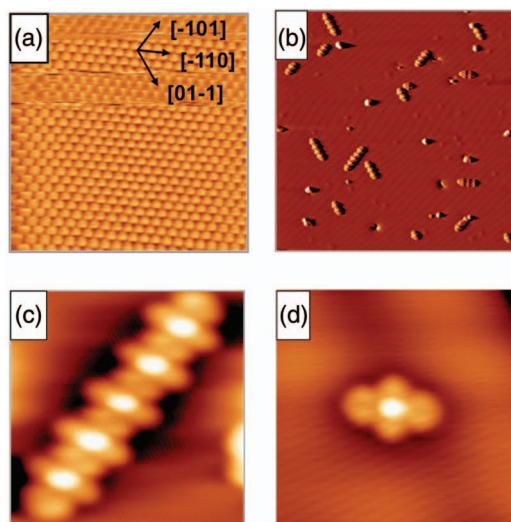


FIG. 1. STM images. (a) $5 \times 5 \text{ nm}^2$ topographic image of clean Ag(111). Scanning parameters are current (I) = 2.0 nA and sample bias voltage (V_s) = 6.8 mV. (b) $50 \times 50 \text{ nm}^2$ differentiated image of Ag(111) with 0.01 ML S at 4.7 K. $I = 0.32 \text{ nA}$, $V_s = -1.1 \text{ V}$. (c) $5 \times 5 \text{ nm}^2$ topographic image of a chain. $I = 0.37 \text{ nA}$, $V_s = -0.69 \text{ V}$. (d) $5 \times 5 \text{ nm}^2$ topographic image of a monomer. $I = 2.1 \text{ nA}$, $V_s = 7.6 \text{ mV}$.

The Ag(111) sample was held at 300 K during S_2 exposure to ensure dissociative adsorption of S_2 , then cooled to 4.7 K for observation. In some experiments, it was re-heated to 200–300 K and re-cooled to 4.7 K; this treatment made no difference in the observations. Furthermore, at 4.7 K, the features observed were purely static; there was no evidence of motion or rearrangement. Thus, the features observed at 4.7 K must have formed at higher temperature.

An STM image of clean Ag(111) is shown in Fig. 1(a). Fig. 1(b) shows a typical STM image after adsorption of 0.01 monolayer (ML) sulfur at 300 K, followed by cooling to 4.7 K. The most striking features are “chains” of variable length but constant width. One is shown at higher magnification in Fig. 1(c). These chains are always oriented with their long axis parallel to one of the three $\langle -110 \rangle$ directions. The shortest chain unit, a monomer, is shown in Fig. 1(d).

These high-quality, high-magnification images reveal that the chains consist of cross-like units, each unit having a bright central protrusion and diamond-like lobes. (We call lobes that span the short width of the chain “equatorial” and the others “axial.”) The chains can be regarded as inorganic polymers. In the direction of the long axis, two-unit chains are significantly shorter than twice the length of a single unit, so the two-unit chains are not simply stacked monomers. Rather, each pair of units shares an axial link between the central protrusions. In multiple-unit chains, the central protrusion-to-central protrusion separation is 4 to 5 times the Ag(111) surface lattice constant. (The uncertainty is due to drift and possible slight miscalibration of XY piezo-electrics in STM.)

We have analyzed a large number of possible structures and compositions with density functional theory (DFT), using the Vienna *Ab initio* Simulation Package (VASP) code,^{22–24} with the Perdew-Burke-Ernzerhof (PBE) approximation²⁵ for exchange-correlation functional. We have identified a few

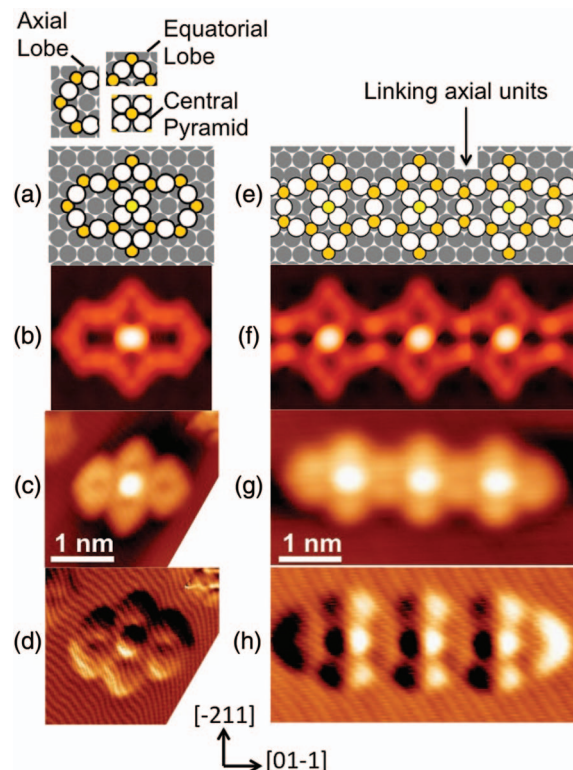


FIG. 2. Simulated and measured STM images. In panels (a) and (e), small yellow circles are sulfur atoms. Large white circles are cluster Ag atoms. Large gray circles are Ag atoms in the Ag(111) surface. (a) $\text{Ag}_{16}\text{S}_{13}$ monomer model. (b) STM image predicted from monomer model, with (9×9) supercell, $(2 \times 2 \times 1)$ k-points, and 2 Ag layers. (c) Measured STM image at same spatial scale and crystallographic orientation as in panels (a) and (b). The image is distorted due to drift. $I = 0.05 \text{ nA}$, $V_s = 1.0 \text{ V}$. (d) Differentiated version of image in panel (c). (e) Chain model. (f) STM image predicted from chain model, with (5×8) supercell, $(2 \times 2 \times 1)$ k-points, and 4 Ag layers. (g) Measured STM image at same scale and orientation as in panels (e) and (f). $I = 1.0 \text{ nA}$, $V_s = -0.5 \text{ V}$. (h) Differentiated version of image in panel (g).

candidates that satisfy all of the following requirements: (1) Close fit between shape and size of the electron density contours in the model (Tersoff-Hamman method) and in the STM images; (2) Long axis of cluster oriented parallel to the close-packed directions of Ag(111); (3) Low chemical potential of sulfur, μ_S .

Within these constraints, a family of related clusters emerges as good candidates. Consider first the monomer. The favored structure is an $\text{Ag}_{16}\text{S}_{13}$ cluster, shown in Fig. 2(a). At its center is a square pyramid, with 4 Ag atoms at the base in the shape of a slightly-distorted square [incommensurate with the underlying Ag(111) substrate], and a S atom at the apex. This pyramid is the central protrusion observed in the STM images, and it is a defining feature of the family of favorable structures. Its stability can be understood in terms of the very strong affinity of S for four-fold hollow sites on Ag. It resembles the basic structural unit of a S-induced reconstruction on Ag(100).⁵ On opposite sides of the Ag_4S pyramid, in $\langle -211 \rangle$ directions, lie 2 small rings comprised of alternating Ag and S atoms. These would be the equatorial lobes in STM. In the $\langle -110 \rangle$ directions, there are 2 larger rings of Ag-S-Ag-S atoms, which would be the axial lobes. The predicted STM

image for this monomer model compares well with the measured image, as shown in Figs. 2(b)–2(d).

For the multiple-unit (polymeric) chains, the corresponding model is shown in Fig. 2(e). The pyramids are linked by new Ag-S units that essentially replace the axial lobes of the 2 erstwhile monomers. The projected image and STM image of the chain are reasonably similar (compare Figs. 2(f)–2(h)). Models that provide better fits with the data may yet be found, but it is likely that any such would be closely related to the structures shown in Fig. 2, particularly in terms of the Ag₄S pyramid as a central building block.

We note that the Ag(111) substrate is minimally perturbed by the presence of the chains, according to DFT. This is consistent with our other DFT investigations of other S-related phases on Ag(111), where we have found that adsorbed atomic S can induce large displacements in the surface Ag layer. However, such configurations are always less favorable than S-Ag clusters that exist on top of an essentially intact Ag(111) substrate. For example, in our study of the ($\sqrt{7} \times \sqrt{7}$)R19° phase of S on Ag(111) at 3/7 ML S coverage, Ag₃S₃ clusters on a relatively unperturbed Ag(111) surface are more energetically favorable than a competing structure in which three S atoms induce reconstruction of the Ag(111) surface.^{15,19} The weak perturbation of the Ag(111) surface implies that the cluster-surface interaction is weak, while Ag-S bonding within the cluster is strong.

Having identified a reasonable structural model, we now comment on the *kinetics and thermodynamics of chain formation*. Steps may play a role in catalyzing or assisting chain formation, because S atoms preferentially decorate step edges on Ag(111) before occupying sites on terraces. Fig. 3(a) is an STM image, showing an Ag(111) step decorated by bright dots that we assign as S atoms. The dots are about 0.58 nm apart, which is twice the Ag-Ag separation along the steps, indicating that S atoms occupy every other site. We also con-

firmed this preference by DFT.¹⁰ The main point is that S concentration is much higher at steps than on terraces when total S coverage is low, as it is in these experiments, because step sites are energetically favored over terrace sites. We propose that this high S concentration at steps facilitates formation of the S-rich chains.

Most steps have the appearance of Fig. 3(a), but a few are decorated with other types of structures. Examples are shown in Fig. 3(b). These other decorations grow out from the lower step edge, often forming a single or double zig-zag-like row of material. These are probably sulfur-induced reconstructions of the step edge.

Sometimes chains are attached directly to steps, in which case they extend out onto the lower terrace, making an angle of 60° or 120° with the step edge, parallel to a close-packed direction of the Ag substrate. [Note that the segment of the step connected to the chain is aligned with the third close-packed direction of Ag(111).] A chain attached to a step is shown in Fig. 3(c). In this particular example, the chain is attached to a reconstructed area of the step, but chains can be found at a variety of step decorations.

There is some evidence that the isolated chains on a terrace may adopt a preferred orientation of 60° or 120° with the nearest ascending step edge. In Fig. 3(d), there are two steps oriented mainly along the $[-110]$ direction. Most of the chains are oriented along the other two close-packed directions, with only a few parallel to $[-110]$. A similar trend can be seen in Fig. 1(b), where there are very few near-horizontal chains or monomers, suggesting that a $[-110]$ -aligned step is close by.

We caution that the available data are not statistically adequate to reach a definitive conclusion about the distribution of terrace chain orientations with respect to step edges, and that this topic warrants further investigation. However, if preferred orientations of 60° or 120° exist, they could be explained with the following model. Chains form at step edges, with favored angles of 60° and 120°. Eventually, the chains separate from the steps and diffuse onto the terraces (at higher temperature than 4.7 K), but they retain their original orientation. Diffusion of the intact chain could be facilitated by the relatively weak interaction between the chain and the Ag(111) substrate, noted above.

The chain length distribution is also of interest. Consider a simple equilibrium model, where the chains are built of n repeated units (each unit denoted by C), stabilized by a neighboring attraction $\phi_C < 0$ between units. If the chain energy E_n varies linearly with n , then the population of chains of length n satisfies $P_n \approx \theta_C \exp[-\phi_C/(k_B T)] P_{n-1}$, so P_n should decay exponentially. Here, $\theta_C \ll 1$ reflects the low equilibrium concentration of units C due to the small amount of excess S (above that decorating steps) on the surface. The logarithm of P_n vs. n (for chains which are well separated from steps, and which are not pinned by any obvious defects) is shown in Fig. 4. The variation is somewhat nonlinear. This may be due to limited statistics, or the kinetics of chain formation at steps. Perhaps, the probability of forming longer chains is limited by the concentration and mobility of sulfur in the local vicinity of the nascent chain along the step edge. In other words, perhaps a step edge is kinetically limited in its ability to “feed”

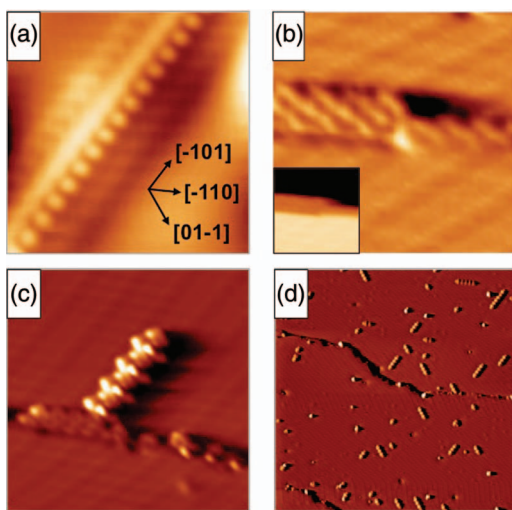


FIG. 3. STM images showing phenomena at steps. In all panels, tunneling conditions are $I = 0.30$ nA and $V_s = -1.0$ V. (a) A 5×5 nm² topographic image of sulfur atoms at a step edge. (b) A 5×5 nm² differentiated image of step reconstruction. Topographic image is shown in the inset. (c) A 10×10 nm² differentiated image showing a chain attached to a step. (d) A 75×75 nm² differentiated image showing chain orientations in the vicinity of ascending steps.

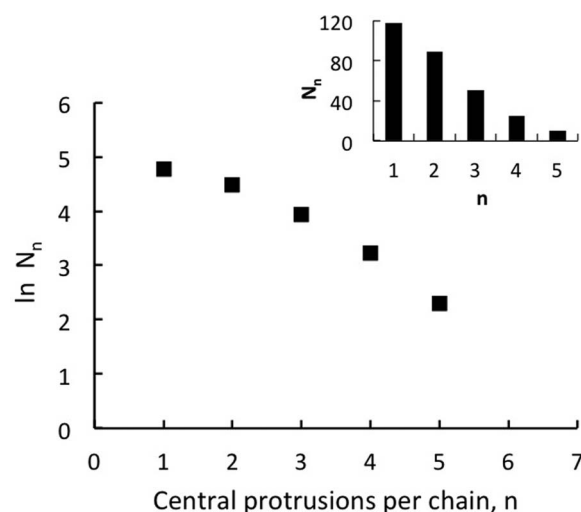


FIG. 4. Semi-log plot of the distribution of chain lengths, N_n , for chains on terraces. In this distribution, chains are only included if they are well separated from steps and not pinned by any obvious defects. The inset shows the raw data.

a growing chain, which could favor detachment over growth for longer chains.

In conclusion, our studies reveal the existence of an entire ensemble of linear nanoscale Ag-S complexes of various lengths on an Ag(111) surface at low coverage and low temperature. There have been various suggestions of the existence of metal-S or metal-O complexes on surfaces, but no observations of such individual isolated moieties for softer metals where they are presumably too dynamic to be imaged under normal conditions. Our use of ultra-low temperature imaging resolves this difficulty. In addition, the STM studies provide a window into formation of the complexes, which appears to occur at steps on the surface decorated with S adatoms, and into the extent of equilibration. However, it should be noted that both formation and equilibration occur at temperatures higher than the temperature of observation. DFT analysis leads to a detailed structural model of the chains, in which the core of the building block is an Ag_4S pyramid.

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